Formation of Nitrosamines in Alkaline Conditions: a Kinetic Study of the Nitrosation of Linear and Cyclic Secondary Amines by Nitroalkanes

Emilio Calle, Julio Casado,* José L. Cinos, Francisco J. García Mateos and Manuel Tostado
Departamento de Química física, Facultad de Química, Universidad, E-37008 Salamanca, España

A study has been made of the nitrosation of sixteen secondary amines, six alkylamines (dimethylamine, diethylamine, dipropylamine, diisopropylamine, dibutylamine, diisobutylamine) and ten cyclic secondary amines (2-methylaziridine, azetidine, pyrrolidine, piperidine, 2-methylpiperidine, homopiperidine, heptamethyleneimine, piperazine, 1-methylpiperazine and morpholine) by nitropropane and nitrobutane in a strongly basic medium ($[OH^-] = 0.1$ mol dm^{-3}). The nitrites were not formed *in situ* (*i.e.* in the actual bulk of the reaction medium) but rather were isolated, purified and used in pure form. The rate equation (i) was found.

$$v = k_{2obs}[\text{amine}][\text{nitrite}] \quad \text{(i)}$$

The fitting of the experimental results to the Taft correlation points to a nucleophilic attack on nitrite esters by the amines. Analysis of the log k_2/pK_a and log $k_2/E_i(v)$ correlations indicates orbital control of the reactions studied. These results, together with the fact that the reactivity of the different amines diminishes ostensibly when the values of the ^{13}C–H nuclear spin coupling constant in the series of corresponding cycloalkanes increase, show that the overall hybridization of the nitrogen atom in the cycle changes from sp^2 in the triangular nucleophile methylaziridine to sp^3 in larger cycles.

The results obtained at different temperatures and with water–tetrahydrofuran media, together with a study of isotope effects suggest that these reactions occur through a highly ordered transition state and that the role of solvation should not be overlooked.

The chemistry of nitrosamines is receiving increasing attention owing to the toxicity[1] and carcinogenic,[2] mutagenic,[3] and teratogenic[4] properties of these compounds. Alkyl nitrites are among those agents responsible for nitrosamine-forming reactions,[5] and a study of the mechanisms of these reactions is interesting for two reasons: (i) from the biological point of view, because of their possible participation in processes that precede carcinogenesis, either by direct contact with the nitrite esters (see, *e.g.* refs. 6 and 7), or with species responsible for their formation present in the human diet (nitrates, nitrites and alcohols, the last being particularly important in nitrosation mechanisms; see *e.g.* refs. 5 and 8) and (ii) from a kinetic viewpoint, since, unlike the situation occurring in nitrosation by other agents, where the mechanism is controlled by physical processes (diffusion),[9] the reaction rate of nitrosation by nitroalkanes is thought to depend on the chemical structure of nitrosatable nucleophiles.

In previous work[10,11] it has been shown that in nitrosation by nitroalkanes, the active substrate is the free amine. This means that alkaline media (not infrequent in human organs such as the intestine or the pancreas, and in some human fluids such as saliva and urine) are particularly favourable to the course of nitrosation reactions. Since Oae *et al.*[12,13] studied the hydrolysis and aminolysis of alkyl nitrites there have been two main limitations to research on nitrosation by nitrite esters: (i) the role of pH has not been sufficiently analysed[13] and (ii) nitrous esters have been prepared *in situ*, without their isolation, with the consequent risk of the simultaneous participation of other nitrosating agents.[10,11,14] In addition the role of the medium has not been sufficiently studied.

In this paper is reported a kinetic study of the nitrosation of sixteen secondary amines by nitropropane (PrONO) and nitrobutane (BuONO) in a strongly alkaline medium. Six of the nitrosatable species were alkylamines: dimethylamine (DMA), diethylamine (DEA), dipropylamine (DnPA), diisopropylamine (DiPA), dibutylamine (DnBA), diisobutylamine (DiBA); the other ten amines were cyclic: 2-methyl-aziridine (2MAZIR), azetidine (AZET), pyrrolidine (PYRR), piperidine (PIPER), 2-methyl-piperidine (2MPIPER), homopiperidine (HOMO), heptamethyleneimine (HEPT), piperazine (PIP), 1-methylpiperazine (1MPIP) and morpholine (MOR).

Table 1 Kinetic parameters of the alkaline hydrolysis of PrONO and BuONO, at 25 °C, $[OH^-] = 0.1$ mol dm^{-3} and $I = 0.25$ mol dm^{-3}

Alkyl nitrite	$k_2/10^{-4}$ dm^3 mol^{-1} s^{-1}	E_a/kJ mol^{-1}
PrONO	4.9 ± 0.1	27.4 ± 2.5
BuONO	5.4 ± 0.3	24.6 ± 2.6

Results and Discussion

Prior to the kinetic study of the nitrosation reactions, the hydrolysis reactions of the nitrite esters were studied under the same conditions. Table 1 shows the results. Good agreement is observed with the results reported by Challis and Shuker[14] for the hydrolysis of ethyl 2-nitroethyl ether, $k_2 = 8.26\ 10^{-4}$ dm^3 mol^{-1} s^{-1} and the rates of the hydrolysis reaction are clearly seen to be lower than those of nitrosation (*vide infra*), except in the case of morpholine and 1-methylpiperazine where adequate correction was carried out. This result is consistent with the known fact[13] that amines are much more nucleophilic than OH^- ions in their reactions with nitrites since, while in alkaline hydrolysis mechanisms there exists an unfavourable lone pair–lone pair interaction between the nucleophilic OH^- species and the nitrogen atom of the nitrites, this does not occur in the aminolysis reaction.

Table 2 Rate constants of the nitrosation reaction of secondary amines by PrONO, k_{2Pr} and BuONO, k_{2Bu}, at 25 °C; $[OH^-] = 0.1$ mol dm^{-3} and $I = 0.25$ mol dm^{-3}; range of initial concentrations, $[PrONO]_0 = (3.6–8.4) \times 10^{-3}$ mol dm^{-3} $[BuONO]_0 = (3.6–6.5) \times 10^{-3}$ mol dm^{-3}, $[nucleophile]_0 = (3.6–42.0) \times 10^{-3}$ mol dm^{-3}

Nucleophile	k_{2Pr}	k_{2Bu}	Nucleophile		$J(^{13}C–H)$
	10^{-3} dm^3 mol^{-1} s^{-1}		pK_a	E_i(v)/eV	Hz[j]
1 DMA	66.4 ± 0.7		10.73[a]		
2 DEA	12.5 ± 0.3		10.93[a]		
3 DnPA	13.6 ± 0.2		11.00[a]		
4 DiPA	1.47 ± 0.02		11.20[a]		
5 DnBA	21.9 ± 0.2		11.25[a]		
6 DiBA	15.2 ± 0.3		10.59[b]		
7 2MAZIR	*i*	*i*		9.57[e]	161[f,g]
8 AZET	21.3 ± 0.3	18.2 ± 0.3	11.29[c]	9.04[e]	134[g]
9 PYRR	175 ± 3	166 ± 4	11.35[b]	8.77[e]	128[f,g]
10 PIPER	26.0 ± 0.4	31.9 ± 0.4	11.12[b]	8.64[e]	123[f], 124[g]
11 2MPIPER	6.40 ± 0.08	5.59 ± 0.09	10.93[d]		
12 HOMO	314 ± 7	281 ± 3	10.89[b]	8.41[e]	123[g]
13 HEPT	1080 ± 20	8990 ± 10	10.78[b]		122[g]
14 PIP	2.54 ± 0.03	3.06 ± 0.03	10.20[b]		
15 1MPIP	0.280 ± 0.005[h]	0.171 ± 0.003[h]	9.16[d]		
16 MOR	0.0957 ± 0.0016[h]	0.0740 ± 0.0018[h]	8.45[d]		

[a] Ref. 27. [b] Ref. 28. [c] Ref. 32. [d] Ref. 29. [e] Ref. 16. [f] Ref. 30. [g] Ref. 31. [h] Corrected value, taking into account the hydrolysis of the alkyl nitrite. [i] No reaction observed. [j] For the corresponding cycloalkane.

Table 3 Typical kinetic run of the reaction of PrONO (7.00×10^{-3} mol dm^{-3}) with HOMO (1.40×10^{-2} mol dm^{-3}) and BuONO (5.90×10^{-3} mol dm^{-3}) with HOMO 1.18×10^{-2} mol dm^{-3}; $[OH^-] = 0.1$ mol dm^{-3} and $I = 0.25$ mol dm^{-3}, at 25 °C (aqueous solution)

t/min	A_{381}(PrONO)	A_{381}(BuONO)
1	0.122	0.105
2	0.098	0.086
3	0.080	0.073
4	0.066	0.063
5	0.054	0.054
6	0.043	0.047
7	0.040	0.042
8	0.034	0.036

In both cases, nitrosation by PrONO and BuONO, rate equation (1) was found which coincides with those observed (2)

$$v = k_{2obs}[amine][nitrite] \quad (1)$$

$$v = k_2[amine][nitrite]/(1 + [H^+]/K_a) \quad (2)$$

at different acidities[10,11] when, as in the present case, $[H^+] \ll K_a$. Eqn. (2) is based on the following reaction scheme:

$$R_2NH_2^+ \rightleftharpoons R_2NH + H^+ \qquad K_a$$

$$R_2NH + R'ONO \longrightarrow R_2NNO + R'OH \qquad k_2, \text{slow}$$

Table 2 shows the k_2 values found for nitrosation by PrONO and BuONO for each of the substrates studied.

As a typical example, Table 3 shows the kinetic run of two nitrosation reactions by PrONO and BuONO. In order to check the nature of the attack on the alkyl nitrites by the amines, the existence of a Taft correlation was confirmed. Fig. 1 shows a negative slope, *i.e.* a nucleophilic attack on alkyl nitrites by the amines (for $\Sigma\sigma^*$ we used the values proposed by Hall[15]).

Fig. 2 shows a plot of log k_2 values against pK_a for different nucleophiles. It is interesting to note that the non-existence of a linear pK_a dependence of the reaction rates (log k_2) for the secondary amines tested in this investigation supports the idea of the reactions being mainly orbital-controlled (apart from the fact that a good correlation between the values of log k_2 and pK_a would not be expected since nucleophilicity and basicity are not closely related). There are a number of results that support this hypothesis.

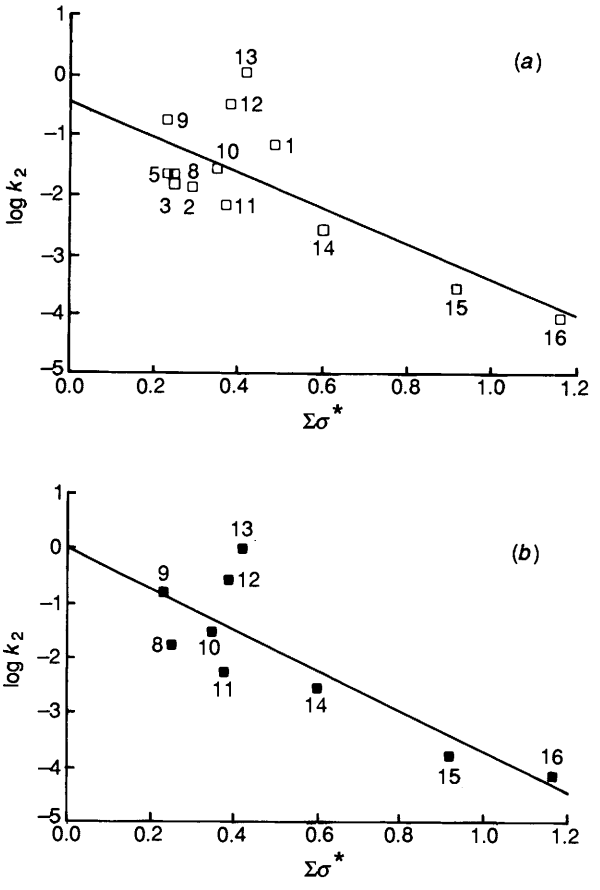


Fig. 1 log k_2 plotted against $\Sigma\sigma^*$ for the reaction of secondary amines with (*a*) PrONO and (*b*) BuONO at 25 °C, $[OH^-] = 0.1$ mol dm^{-3}, and $I = 0.25$ mol dm^{-3}. Amines are numbered as shown in Table 2.

(1) Linearity is observed between log k_2 and the pK_a values (Fig. 3) in the case of the substrates 2MPIPER, PIP, 1MPIP and MOR (to which PIPER can be added). Indeed, as is known,

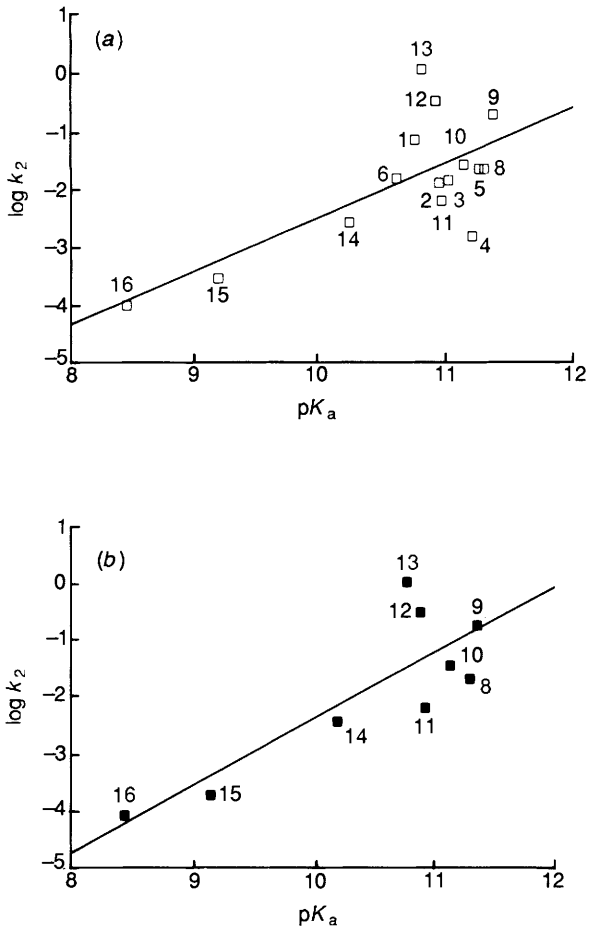


Fig. 2 log k_2 plotted against pK_a of secondary amines for the reactions with (*a*) PrONO and (*b*) BuONO at 25 °C, $[OH^-]$ = 0.1 mol dm^{-3} and I = 0.25 mol dm^{-3}. Amines are numbered as shown in Table 2.

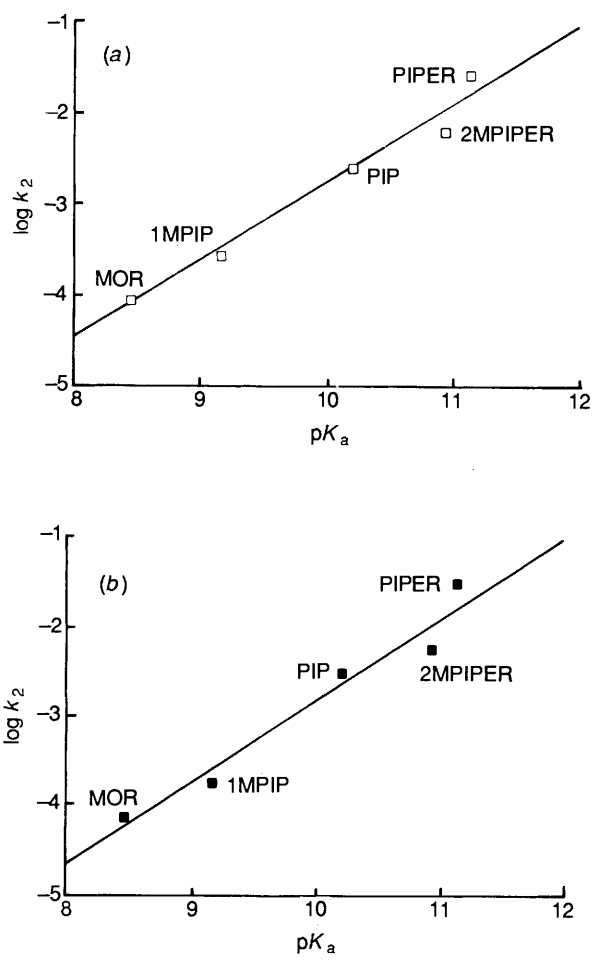


Fig. 3 Plot of log k_2 against pK_a for six-membered cyclic amines (*a*) with PrONO and (*b*) with BuONO

orbital control should reflect a linear dependence between the log k_2 and the vertical ionization potential, E_i(v), of the nucleophiles. Also, since the pK_a values of the structurally similar secondary amines, in good agreement with the Brønsted relationship, are directly proportional to those of the E_i(v),[13] the linearity of log k_2/pK_a can be seen in this particular case as a confirmation of that existing between log k_2 and those of the respective E_i(v) which, unfortunately, are not known.

(2) We do have, however, the E_i(v) values of five of the cyclic amines studied, namely 2MAZIR, AZET, PYRR, PIPER and HOMO. As can be seen in Fig. 4, a study of their nitrosation, by PrONO and BuONO reveals a tendency for the reactivity (k_2) to increase on decreasing the vertical ionization potential.

(3) It is known[16] that in cycloalkanes the s character of the carbon–hydrogen bond increases with decreased ring-size. The value of the nuclear-spin coupling constant of the respective cycloalkanes are reported in Table 2. Particularly noteworthy is the great similarity between the $J(^{13}C-^{1}H)$ values in cyclopropane and in benzene [J(C–H) = 159; *cf.* ref. 17). An explanation for the facts noted in (2) and (3) is readily found in the overall hybridization of the nitrogen atom of the cycle; that is, a change of the lone-pair from an sp^2 hybrid in methylaziridine to sp^3 in larger cycles.

Table 4 shows the variation of k_2 with the composition of water–THF medium in the nitrosation reactions of the five cyclic amines seen to react (with 2MAZIR no reaction was observed). Table 5 shows the values of the activation parameters found on application of the Eyring–Wynne–Jones equation to the nitrosation reaction of the same five nucleophiles in aqueous and water–organic media. The rate constant can be seen to fall

Table 4 Rate constants of the nitrosation reaction of secondary amines by PrONO in aqueous and water–THF media, at 25 °C; $[OH^-]$ = 0.1 mol dm^{-3} and I = 0.25 mol dm^{-3}; $[\text{nucleophile}]_0$ = 1.40 × 10^{-2} mol dm^{-3}, and $[\text{PrONO}]_0$ = 7.00 × 10^{-3} mol dm^{-3}

	k_2/10^{-3} dm^3 mol^{-1} s^{-1}		
Nucleophile	H_2O	0.50 mol dm^{-3} THF	1.00 mol dm^{-3} THF
AZET	21.3 ± 0.3	13.1 ± 0.2	12.5 ± 0.1
PYRR	175 ± 3	134 ± 7	124 ± 4
PIPER	26.0 ± 0.4	22.0 ± 0.9	20.4 ± 0.2
HOMO	314 ± 7	230 ± 9	202 ± 5
HEPT	1080 ± 20	470 ± 8	437 ± 3

with the polarity of the medium, suggesting that the two neutral reagents combine to form a polar transition-state complex;[18] this result is consistent with those found in comparable situations (see, for example, refs. 10, 11, 13 and 19). The high negative values of the activation entropy show that this complex must have a high degree of organization. Similar results are obtained in the case of the nitrosation by BuONO.

The role of solvation in the mechanism studied was also analysed. The high value of the β parameter in an aqueous medium (0.76 with PrONO, 0.82 2ith BuONO) contrasts with that found by Oae[13] *et al.*, β = 0.58, in his study of the nitrosation of sterically similar amines. Disregarding Oae's failure to consider the effect of the medium (which does not allow these authors to propose a rate equation), and given that in our conditions (i) the amines showing satisfactory fulfilment of the Brønsted correlation are also sterically similar and (ii) the

Table 5 Activation parameters for the nitrosation reaction of secondary cyclic amines by PrONO in aqueous and water–THF media; temperature range 8–25 °C ($\Delta H^{\ddagger}$ in kJ mol^{-1}; $\Delta S^{\ddagger}$ in J mol^{-1} K^{-1})

	H_2O		0.5 mol dm^{-3} THF		1.00 mol dm^{-3} THF	
Nucleophile	$\Delta H^{\ddagger}$	$-\Delta S^{\ddagger}$	$\Delta H^{\ddagger}$	$-\Delta S^{\ddagger}$	$\Delta H^{\ddagger}$	$-\Delta S^{\ddagger}$
AZET	31.4 ± 1.4	171 ± 32	33.3 ± 1.4	169 ± 21	34.6 ± 1.8	165 ± 30
PYRR	39.2 ± 1.5	128 ± 10	28.9 ± 1.2	164 ± 21	22.7 ± 1.0	186 ± 30
PIPER	43.2 ± 0.9	130 ± 6	38.9 ± 1.9	146 ± 18	41.1 ± 1.0	139 ± 8
HOMO	37.2 ± 1.7	130 ± 11	27.7 ± 0.9	164 ± 15	29.3 ± 0.8	160 ± 12
HEPT	30.3 ± 1.7	143 ± 16	26.9 ± 0.6	161 ± 18	24.7 ± 0.6	169 ± 11

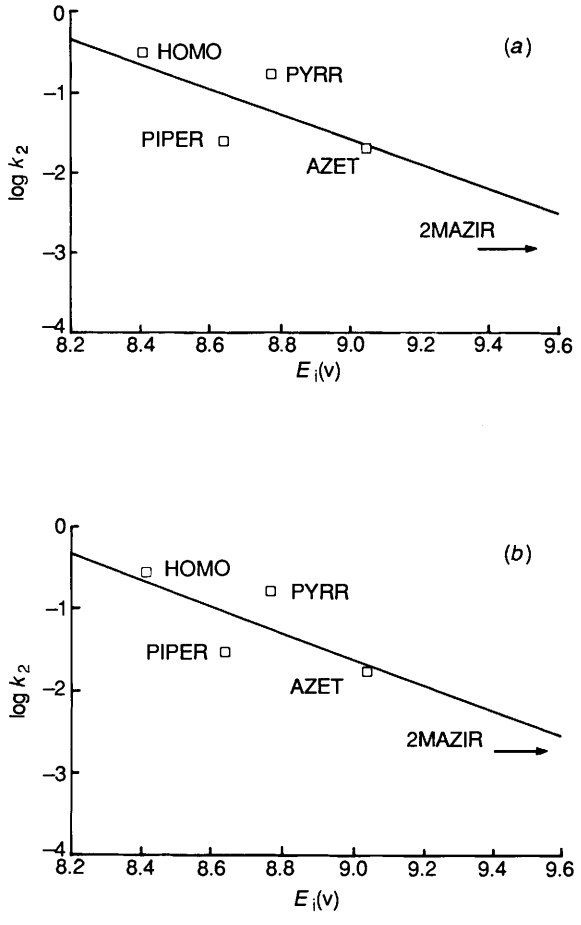


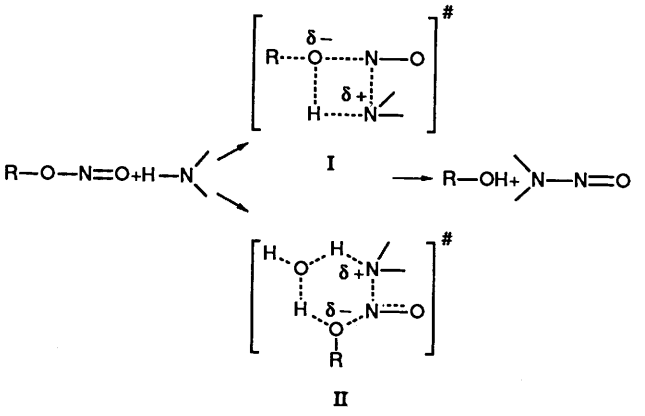
Fig. 4 Plot of log k_2 against E_i(v) in the nitrosation of secondary amines with (*a*) PrONO and (*b*) BuONO

value of β decreases with the decreased polarity of the medium, it should then be suspected that these effects would be due to changes in the solvation. Keeping in mind that the value of the β parameter represents the extent of bond formation in the transition state[20,21] and the theoretical predictions of when kinetic changes occur along the proton transfer reaction coordinate with bases of different size,[22] the above-described results can be rationalized. According to Kurz,[22] when such bases are small (H_2O, for example), changes in solvation should be coupled with proton transfer, and the mechanism should be synchronous. When the bases are large, a stepwise mechanism should be favoured in which the solvent first reorganizes to a configuration appropriate for the transition state, the proton is transferred, and the solvent then relaxes to its product configuration.[23] This may be the cause both of the higher value of the β parameter found in this work when compared with that measured by Oae *et al.* for 61% dioxane solutions, and of the decrease of the β value when the proportion of THF in the reaction medium is increased.

Table 6 Values of k_{2H}/k_{2D} in the nitrosation of piperidine by PrONO in aqueous and water–THF media, at 25 °C; $[OH^-]$ = 0.1 mol dm^{-3} and I = 0.25 mol dm^{-3}; $[PIPER]_0 = 1.49 \times 10^{-2}$ mol dm^{-3}, and $[PrONO]_0$ = 7.45 10^{-3} mol dm^{-3}

Reaction medium	k_{2H}/k_{2D}
Water	1.7
Water–THF (1.00 mol dm^{-3})	1.3

The determination of an isotope effect on the nitrosation reaction (Table 6) supports the hypothesis of a cyclic structure for the highly ordered intermediates (*cf. e.g.* refs. 10, 11 and 13). The decrease observed in the k_{2H}/k_{2D} ratio in the presence of THF in the reaction medium (although maintaining values higher than unity) can be viewed as a test of the effect of proton transfer on the mechanism studied.[24] This would mean that the readily solvated reagents (the amine in particular) would favour proton transfer in the actual formation of the nucleophile/electrophile bond (see, *e.g.* ref. 25). If this were so, the k_2 values would be higher in water than in water–THF media as, in fact, has been observed (see Table 4). In this context, structures like **II** (once proposed by Oae *et al.*[13]) would exist in an aqueous medium, while structures like **I** would be suited to water–THF media (and, of course, to reactions occurring in the absence of water). On the other hand, and since structure **I** is more rigid than **II**,



the absolute values of $\Delta S^{\ddagger}$ should change when the amount of THF in the reaction medium changes. As well as confirming the non-negligible effect of the solvation term in the formation of the transition state, the experimental results shown in Table 5 are consistent with such a hypothesis.

Experimental

Both nitropropane and nitrobutane were prepared by a standard procedure[26] from corresponding alcohols (Panreac, PA grade) and sodium nitrite (Panreac, PA grade) in dilute sulfuric

acid (Panreac, PA grade). Once the nitrite had been separated by decantation it was distilled twice. The amines DMA, DEA, DnPA, DiPA, DnBa, PYRR, PIPER, 2MPIPER, HOMO, PIP, 1MPIP and MOR were from Merck (PA grade), DiBA was from Fluka (PA grade), and 2MAZIR, AZET and HEPT were from Aldrich (PA grade). Tetrahydrofuran (Panreac, PA grade) was distilled from metallic sodium before use.

The alkaline medium consisted of 0.10 mol dm^{-3} NaOH (Merck, PA grade). The ionic strength (0.25 mol dm^{-3}) was adjusted by addition of sodium perchlorate (Merck, PA grade). The heavy water (99.77%) in which the reagents were prepared was from the *Centro de investigaciones energéticas, medioambientales y tecnológicas, CIEMAT*, Spain. For the measurement of the reaction rate, a spectrophotometric technique was used. The absorbance, A, of nitrite esters was determined at 381 nm ($\varepsilon_{PrONO} = 24.7 \pm 0.4$ dm^3 mol^{-1} cm^{-1}; $\varepsilon_{BuONO} = 21.8 \pm 0.5$ dm^3 mol^{-1} cm^{-1}) where none of the other intervening species absorb.

For the measurement of the reaction kinetics, alkyl nitrites were used as the control species. This method has the following advantages over the usual one of following the nitrosamine formed: (i) the same technique can be used for the kinetic study of the hydrolysis of the nitrite esters under the same working conditions, (ii) it avoids the need to neglect the absorption of the alkyl nitrites themselves as compared with that of the nitrosamine product (as is done when the latter is used as a control species; *cf. e.g.* ref. 10) and (iii) the problem of the determination of A_∞ is resolved.

Spectrophotometric measurements were carried out on a Shimadzu 240 VIS–UV apparatus with a constant-temperature cell holder (±0.1 °C); pH measurements were carried out using a digital Radiometer Model M64 with a GK2401B combined electrode.

The kinetic results were analysed by the integration method and good second-order kinetic behaviour was found under all conditions tested. Each reported k_2 value is the mean of at least three or four separate determinations.

Acknowledgements

J. C. thanks the Spanish *Comisión Interministerial de Ciencia y Tecnología, CICYT*, for supporting the research reported in this paper as part of an investigation on the precursor mechanisms of carcinogenesis by *N*-nitroso compounds (Grants No. PA86/0111 and ALI389/90). Thanks are also due to the Commission of the European Communities for their support (SCIENCE Plan, Contract No. SC1000408).

References

1 J. M. Barnes and P. N. Magee, *Br. J. Ind. Med.*, 1954, **11**, 167.
2 C. E. Searle, ed., *Chemical Carcinogens*, American Chemical Society Monographs No. 182, 2nd edn., Washington DC, 1985.
3 F. K. Zimmermann, *Biochem. Pharmacol.*, 1971, **20**, 985.
4 H. Druckrey, *Xenobiotica*, 1973, **3**, 271.
5 D. L. H. Williams, *Nitrosation*, Cambridge University Press, Cambridge, 1988.
6 J. J. Taylor, *Food Additives*, Wiley, New York, 1984.
7 A. R. Butler, *Chem. Br.*, 1990, **26**, 419.
8 J. Casado, F. M. Lorenzo, M. Mosquera and M. F. Rodríguez Prieto, *Can. J. Chem.*, 1984, **62**, 136.
9 J. Casado, A. Castro, J. R. Leis, M. A. López Quintela and M. Mosquera, *Monatsh. Chem.*, 1983, **114**, 639.
10 J. Casado, A. Castro, F. M. Lorenzo and F. M. Meijide, *Monatsh. Chem.*, 1986, **117**, 335; *cf.* also, J. Casado, ed., *Proceedings of the Bilateral Hispano-British Seminar on Mechanisms of Formation of Carcinogen Nitroso Compounds*, Vigo, Spain, 1982, in *Acta Cient. Compost.*, 1982, 19 (1–2).
11 J. Casado, A. Castro, M. A. López Quintela and F. M. Lorenzo Barral, *Bull. Soc. Chim. Fr.*, 1987, 401.
12 S. Oae, N. Asai and K. Fujimori, *J. Chem. Soc., Perkin Trans. 2*, 1978, 571.
13 S. Oae, N. Asai and K. Fujimori, *J. Chem. Soc., Perkin Trans. 2*, 1978, 1124.
14 B. C. Challis and D. E. G. Shuker, *J. Chem. Soc., Chem. Commun.*, 1979, 315.
15 H. K. Hall, *J. Am. Chem. Soc.*, 1957, **79**, 5441.
16 K. Yoshikawa, M. Hashimoto and I. Morishima, *J. Am. Chem. Soc.*, 1974, **96**, 288.
17 L. M. Jackman and S. Sternhell, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd edn., Pergamon, London, 1969.
18 K. J. Laidler, *Cinética de reacciones*, Alhambra, Madrid, 1966, Vol. II.
19 Z. Kricsfalussy and A. Bruylants, *Bull. Soc. Chim. Belg.*, 1964, **73**, 96.
20 N. B. Chapman and J. Shorter, eds., *Correlation Analysis in Chemistry*, Plenum Press, New York, 1978.
21 L. Albuquerque and R. Gonçalves, *Cinética química*, Escolar, Lisboa, 1986.
22 J. L. Kurz and L. C. Kurz, *J. Am. Chem. Soc.*, 1972, **94**, 4451.
23 A. Kresge, *Chem. Soc. Rev.*, 1973, **2**, 475.
24 V. J. Shiner, Jr., *Isotope Effects in Chemical Reactions*, eds. C. J. Collins and N. S. Bowman, Van Nostrand Reinhold, New York, 1970.
25 B. K. Carpenter, *Determination of Organic Reaction Mechanisms*, Wiley-Interscience, New York, 1984.
26 W. A. Noyes, *Org. Synth.*, Coll. Vol. II, 1943, 108.
27 J. J. Christensen, R. M. Izatt, D. P. Wrathall and L. D. Hansen, *J. Chem. Soc. A*, 1969, 1212.
28 V. Frenna and N. Vivona, *J. Chem. Soc., Perkin Trans. 2*, 1985, 1865.
29 F. M. Lorenzo Barral, Ph.D. Thesis (Sp), Universidad de Santiago, Spain, 1985.
30 N. Muller and D. E. Pritchard, *J. Chem. Phys.*, 1959, **31**, 768, 1471.
31 C. S. Foote, *Tetrahedron Lett.*, 1963, **9**, 579.
32 S. Searles, M. Tamres, F. Block and LL. A. Quarterman, *J. Am. Chem. Soc.*, 1956, **78**, 4917.

Paper 1/05734K
Received 12*th November* 1991
Accepted 18*th February* 1992